Supporting Information

Facile Fabrication of Degradable Polyurethane Thermosets with High Mechanical Strength and Toughness via the Cross-linking of Triple Boron-Urethane Bonds

Chunyang Bao*, Xuhao Zhang, Pengdong Yu, Qingzhong Li, Yusheng Qin, and Zhirong Xin*

College of Chemistry & Chemical Engineering, Yantai University, Yantai 264005, China

Materials. Poly(tetramethylene ether glycol) (PTMEG-1000, $M_n = 1000$ g/mol), Hexamethylene diisocyanate (HDI), Dibutyltin dilaurate (DBTDL), Boric Acids (BA), 1,1,1-tris(hydroxymethyl)propane (TMP), and Triethylamine (TEA) were purchased from Aladdin. Dry N, N-dimethylacetamide (DMAC) was purchased from Energy Chemical. Tetrahydrofuran (THF) and Hydrochloric Acid (HCl, 36%-38%) were purchased from Beijing Chemical Reagent Company, China. All chemical compounds were used without further purification.

Characterization. ¹H NMR spectra were measured using a 500 MHz Bruker instrument. FT-IR spectra of the linear PU samples were taken on a Bruker VERTEX 80V FT-IR spectrometer. The FT-IR spectra of PTMEG-HDI-BA $_x$ samples were performed on a Bruker FT-IR spectrometer in ATR mode between 400 and 4000 cm⁻¹ at room temperature. The thermal stability analysis was determined on a TA Instruments Q500 Thermogravimetric analyzer under the nitrogen atmosphere. Each sample (~10 mg) was heated from 25 to 800 °C with a rate of 10 °C/min. DMA measurements were carried out on a Dynamic Mechanical Analyzer TA Instrument Q800 using tension film mode with a frequency of 1 Hz and strain amplitude of 1%. The temperature ramp ranged from -100 to 120 °C with a heating rate of 5 °C/min. DSC measurements were conducted on a Mettler Toledo STARe system at a heating and cooling speed of 20 °C/min in N2 atmosphere. All the stress-strain curves were performed on a 410R250 Tension Instrument (TEST RESOURCES Inc., USA) with a stretching speed of 50 mm/min at a temperature of 22 °C and relative humidity of ~20%. For the tensile test, the PTMEG-HDI-BA_x samples were cut into dumbbell shape (12) $mm \times 2 mm \times 0.4 mm$). Young's modulus values were determined by the slope of the stress-strain curve in the initial linear region within the strain of 5%. The toughness is defined as the area surrounded by the stress-strain curves.

Swelling Tests. Sol fraction and swelling ratio were determined by equilibrium swelling experiment in THF based on Flory-Rehner equation. Equilibrium swelling experiments were conducted by immersing PTMEG-HDI-BA_x in THF at room temperature for 72 h, and the solvent is replaced with fresh solvent for each 24 h. After swelling, the solvent was wiped off quickly from the sample surface using filter paper,

and the samples were immediately weighed and then dried in a vacuum oven at 60 °C until constant weight. Three specimens were measured for each sample. The swelling ratio is defined as $(m_1-m_2)/m_2$, and sol fraction is determined as $(m_0-m_2)/m_0$, where m_0 is the sample mass before swelling, m_1 and m_2 are the weights of the swollen and deswollen samples, respectively.



Figure S1. Synthesis route of PTMEG-HDI-TMP_{1.5}.

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Samples	PTMEG	HDI	BA	TMP
PTMEG-HDI-	3 mml	6.6 mml	2.4 mml	0 mml
BA _{2.2}				
PTMEG-HDI-	3 mml	5.4 mml	1.6 mml	0 mml
$BA_{1.8}$				
PTMEG-HDI-	3 mml	4.5 mml	1 mml	0 mml
$BA_{1.5}$				
PTMEG-HDI-	3 mml	4.5 mml	0 mml	1 mml
TMP _{1.5}				

Table S1. Feeding ratios of cross-linked poly(boron-urethanes) and PU.



Figure S2. Swelling ratio and gel content of the cross-linked poly(boron-urethanes) and PTMEG-HDI-TMP_{1.5}.

Table S2. The mechanical properties of cross-linked poly(boron-urethanes) and PU.

Samples	Young's Modulus	Tensile Stress	Tensile Strain	Toughness
	(MPa)	(MPa)	(%)	(MJ m ⁻³)
PTMEG-HDI-	20.98	41.2	1598	350
BA _{2.2}				
PTMEG-HDI-	19.07	50.5	1606	405
$BA_{1.8}$				
PTMEG-HDI-	10.07	53.9	1865	390
$BA_{1.5}$				
PTMEG-HDI-	2.26	19.7	1972	131
TMP _{1.5}				



Figure S3. DSC curves of PTMEG-HDI-BA_{2.2}, PTMEG-HDI-BA_{1.8}, PTMEG-HDI-BA_{1.5}, and PTMEG-HDI-TMP_{1.5}.



Figure S4. TGA curve of the cross-linked PTMEG-HDI-TMP_{1.5}.



Figure S5. The degradation curves PTMEG-HDI-BA_{2.2} in 0.1 M HCl THF solutions at room temperature.



Figure S6. (a) Original PTMEG-HDI-TMP_{1.5} film. (b) PTMEG-HDI-TMP_{1.5} film after immersing in 0.1 M HCl/THF solution for 12 h.



Figure S7. ¹H NMR spectra of the linear PU degraded from the cross-linked PTMEG-HDI-BA_{1.8} (a) and PTMEG-HDI-BA_{2.2} (b).



Figure S8. FT-IR spectra of the linear PU degraded from the cross-linked PTMEG-HDI-BA_{1.8} (red curve) and PTMEG-HDI-BA_{2.2} (black curve).



Figure S9. GPC traces of the linear PU degraded from the cross-linked PTMEG-HDI-BA_{2.2} (black curve), PTMEG-HDI-BA_{1.8} (red curve), and PTMEG-HDI-BA_{1.5} (blue curve).



Figure S10. GPC traces of the linear PU before cross-linking with boronic acid.

	M _n	$M_{ m w}$	PDI
PTMEG-HDI-BA _{2.2}	1300	1500	1.15
PTMEG-HDI-BA _{1.8}	17200	23400	1.37
PTMEG-HDI-BA _{1.5}	32800	55500	1.69
PTMEG-HDI _{2.2}	5300	10500	1.97
PTMEG-HDI _{1.8}	7600	15800	2.07
PTMEG-HDI _{1.5}	57000	93000	1.63

Table S3. molecular weight of the PUs before cross-linking with boronic acid and the linear PUs degraded from the cross-linked poly(boron-urethanes).



Figure S11. Tensile stress-strain curve of linear PU oligomer degraded from PTMEG-HDI-BA_{1.5}.